AD-A185 022 NUCLEOPHILIC DISPLACEMENT REACTIONS OF 4-SUBSTITUTED-12-DINITROBENZENES W.. (U) PRAIRIE VIEW A AND M UNIV TX DEPT OF CHEMISTRY L L COLE ET AL. 1/1

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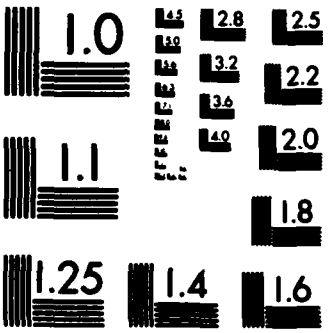

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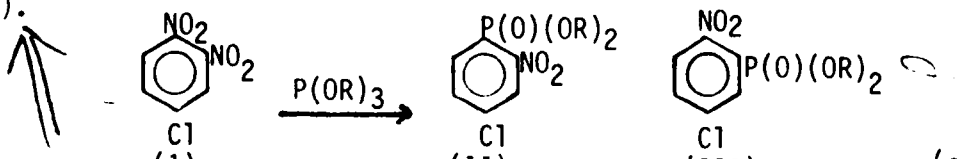
We wish to report the results of studies on the reactions of five different dinitro-compounds with triethylphosphite in the solvent acetonitrile at 3 different temperatures. Therefore, kinetic data has been determined for the reaction of triethylphosphite with 1,2-dinitro-4-chlorobenzene, 1,2-dinitro-4-methylbenzene, 1,2-dinitro-4-methoxybenzene, 1,2-dinitro-4-benzonitrile, and with 1,2,4-trinitrobenzene at 40°, 50°, and 63°C. The products in these reactions are the corresponding diethyl-4-substituted-1- or -2-nitro-phenyl phosphonate esters, II and III (~~fig 1~~). The reactant ~~in figure 1~~ is the 1,2-dinotro-4-chlorobenzene (I).

fig. 1



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The results of our investigation are summarised in the following observations;

1. The order of reactivity for this series of 1,2-dinitro-4-substituted benzenes was shown to be $-NO_2 > -CN > -Cl > -Me > -OMe$. Kinetic data for those reactants with COOH and C(O)OMe in the 4 position are't reported due to possible reactivity between the substituent group and the solvent.

2. Reactants with electron with-drawing groups (NO_2, CN, Cl) in the 4 position gave almost 100% yield the product II, i.e., phosphorus substitution at the 1 position. Reactants with electron donating groups (OMe, Me,) in the 4 position gave a mixture of both phosphate esters (II and III), but with III as the major product. The isomers II and III were resolved and quantitatively determined by g.c.- m.s. analysis.

3. Arrhenius activation energy (E_a), enthalpy of activation ($\Delta H^{\ddagger}$), and entropy of activation ($\Delta S^{\ddagger}$) have been calculated for each of the reactions. Arrhenius activation parameters represent values for phosphorus substitution at the 1 position of each reactant Arrhenius activation parameters are given in Table 1;

Table 1

Activations Enthalpies, Entropies, and Energies for Phosphorus Displacement of a Nitro Group at Position 1

Substitutent at position 4	E_a (kcal/mol)	$\Delta S^{\ddagger}$(eu)	$\Delta G^{\ddagger}$ (kcal/mol)
a. CH_3	19.60	-16.43	23.61
b. O-CH_3	18.84	-18.09	24.14
c. Cl	14.80	-30.84	23.04
d. CN	9.50	-28.01	19.01
e. NO_2	5.23	-31.00	14.31

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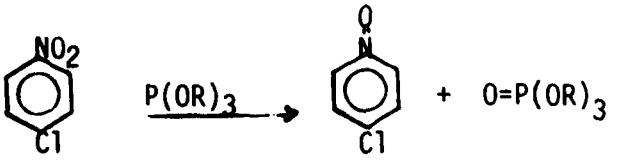
4. The rate data does give a negative Hammett plot with the appropriate sigma values. Therefore the mechanism is pure nucleophilic aromatic substitution even with electron donating groups in position 4 (para). The conclusion is that phosphorus will attack the aromatic ring to remove a nitro group only if an adjacent nitro group is present (ortho). Phosphorus will reduce an aromatic nitro group if an adjacent nitro group is not present. While the presence of electron donating groups tends to increase the rate of the reduction reaction of mononitro-aromatics, they have no effect in promoting reduction with 1,2-dinitro-aromatics. The reduction reaction is shown in figure 2, below.

fig. 2



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